A New Concept for the Fabrication of Hydrogen Selective Silica Membranes

Annual Report

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Abstract

We are attempting to fabricate H_2-selective silica-based films by "layer-by-layer" deposition as a new approach for thin films. A sonication-assisted deposition method was mainly used for "layer-by-layer" deposition. In addition, other approaches such as a dip-coating and the use of a polymer matrix with a layered silicate were contrived as well. This report shows the progress done during the 2nd Year of this award.

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Introduction

As stated in the NRC report on Novel Approaches to Carbon Management, "there is a need for novel membranes that can perform the separation of CO_2 and H_2 at high temperature and pressures." Extensive efforts over the last several decades have explored high temperature H_2-selective membranes made of silica, other oxides, Pd and other metals or alloys, and more recently various zeolite and non-aluminosilicate molecular sieves. Although promising separation results have been reported for many of these technologies, they all suffer from high processing costs for membrane fabrication and long-term stability limitations. In this proposal, we revisit the objective of high temperature H_2-selective membranes with a fresh look and propose to explore a new simple concept for the fabrication of ultra-thin, stable molecular sieve H_2-selective membranes.

This proposal is based on the use of thin films of plate-shaped layered silicate to form H_2 selective membranes.

This simple idea has not been attempted before. The potential advantages of the proposed approach compared to other technologies that are currently under development include :

(1) No need to grow (hydrothermally or by chemical vapor/fluid deposition) the selective layer on the support
(2) Potential for high selectivity and flux
(3) Potential for high stability.

Executive Summary

The primary goal of this project is to make use of crystalline layered silicates to fabricate hydrogen selective membranes for use in high temperature H_2/CO_2 separations. The silicates play a significant role of molecular sieving so that small molecules like H_2 are allowed to pass through silicates, while larger sized molecules such as CO_2 are prohibited and detour around silicates. It is expected that these different pathways make possible H_2/CO_2 separation through layered silicate containing composite membranes.
For Year 2 plan, it was proposed to:

(1) Fabricate multi-layered mesoporous silica-MCM-22 films by repetitions of particle deposition, SiO_2 coating, and calcination
(2) Further, prepare multi-layered mesoporous silica-MCM-22 films on not only α-Al_2O_3 discs but also tubular Stainless Steel supports.
(3) Test single gas permeation to examine the separation performance of H_2/CO_2.

Though some proposed tasks in Year 2 were not completed, a systematic and robust way for multi-layered films was established. It is based on chemical attachment of silicate layers. Furthermore, we worked on other approaches: a) use of simple dip-coating for layered silicate composite film fabrication and b) fabrication of polymer-layered silicate composite membranes. In particular, we compared the effectiveness of different approaches with the chemically deposited layers.

A closely-packed MCM-22 layer is achieved by a newly developed sonication-assisted method (Lee et al., 2005), which may also be suitable in order to scale-up the MCM-22 films (Figure 1). MCM-22 deposition, mesoporous SiO_2 coating, and calcination were repeated up to 2 times. This approach is often described as "layer-by-layer" deposition. It appears that more layers of MCM-22 films are needed to achieve targeted separation performance.

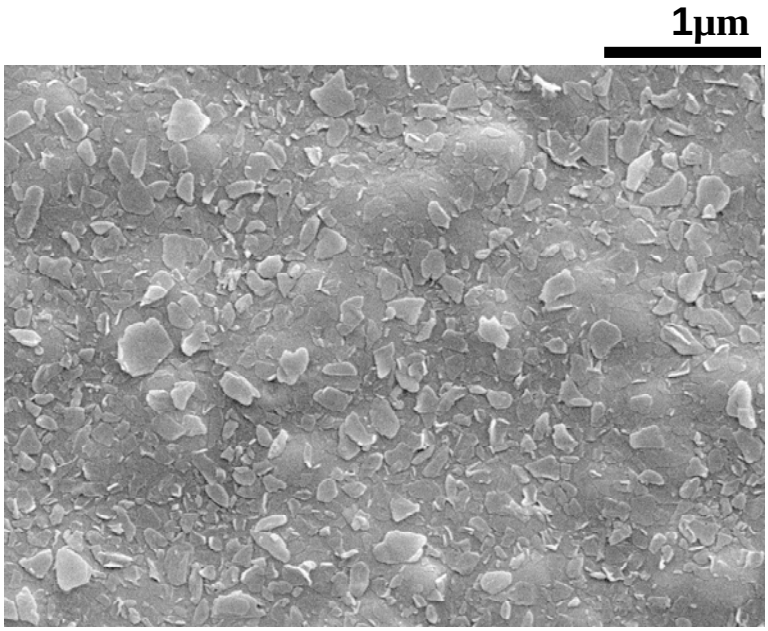

Figure 1. SEM of chemically attached MCM-22 layer on SiO_2 coated porous α-Al_2O_3 support.

Experimental

1. Membrane synthesis

Synthesis of a layered silicate, i.e. MCM-22 (Corma et al., 1998), calcination with agglomeration prohibitor (Wang et al., 2000), functionalization of α-Al_2O_3 discs with 3-chloropropyltrimethoxysilane (3CP-TMS) (Ha et al., 2000; Lai et al., 2003), and silicate particle deposition are described in the 2005 annual report (see page 8 in the Year 1 Annual Report). In year 2 of the project, several membranes were prepared using the above mentioned procedures and are outlined below.

1.1 Sonication-assisted MCM-22 particle deposition and fabrication of mesoporous silica-MCM-22 films

In addition to coating made by reflux described in the Year 1 Annual Report, a recently developed method was adapted to form MCM-22 layer (Lee et al., 2005). The process consists of two steps, which are surface functionalization and sonication-assisted particle deposition, respectively. At first, dried α-Al_2O_3 discs, one side of which had been polished and coated with SiO_2, were placed in glassware while Ar was being fed continuously. Then, ~ 30 ml anhydrous toluene (Aldrich) was poured into the glassware under Ar flow. In addition, 4 ml 3CP-TMS was added by a syringe from a bottle located temporally in an Ar-filled zip lock bag. The entire glassware was heated and refluxed at ~110°C for 4 hours. Then, the α-Al_2O_3 discs were taken out, washed in fresh toluene, and stored in a drying oven (~ 120°C) before particle deposition .

In the mean time, about 0.02g of calcined MCM-22 powder was added to home-made dry glassware under Ar flow. Quickly, ~ 50 ml dry toluene was added. Then 1 hour sonication was done to disperse and possibly break MCM-22 particles in toluene. The functionalized α-Al_2O_3 discs were taken out from the drying oven and stacked between cover glass on both sides. The cover glass sandwiched discs were placed vertically in a comb-shaped Teflon support and inserted in glassware containing MCM-22 dispersion. Then, the sealed glassware is immersed in a sonication bath and sonicated for 10 minutes. Additional 2 minutes sonication was done to horizontally placed discs with SiO_2 coating side facing upward. The MCM-22 deposited discs were taken out of the glassware, washed in fresh toluene, and dried in a drying oven (~ 120°C) before mesoporous SiO_2 coating was done on MCM-22 layer. After mesoporous SiO_2 coating, the discs were heated to 480°C with 1°C/min ramp rate and held for 4 hours under 150ml/min air flow.

1.2. Dip-coated mesoporous silica-MCM-22 films.

First, calcined MCM-22 particles were functionalized with 3-aminopropyltriethoxysilane (3AP-TES, Aldrich) based on a development by Ha et al., 2004, recovered by a centrifuge, and stored in non-humid environment. Specifically, ~1.2 g of calcined MCM-22 powder was added to a two-neck round flask under Ar flow followed by the addition of 200 ml dry toluene. The flask was sonicated for 1 hour, and then the flask was positioned in a silicone oil bath preheated to 110°C. Quickly, 3 ml

3AP-TES was added. The surface functionalization was done in a reflux mode with ~ 350 rpm stirring for 2.5 hours in Ar atmosphere. Functionalized MCM-22 particles (MCM-22 (F)) were recovered by one time centrifugation.

0.3 g of MCM-22 (F) particles were added to 100 ml of 256:1 diluted silica sol contained in a glass jar. The silica sol was produced based on a method in the literature (Lai et al., 2004). The suspension was further sonicated to disperse MCM-22 particles homogeneously. Then, coating was done to the polished side of Al_2O_3 discs by contacting this side on the surface of silica-MCM-22 dispersion. After ~ 20 seconds, the discs were slipped away and dried vertically to evaporate off any ethanol for 40 seconds. The dip-coating was repeated up to 8 times. All the samples were calcined before the single gas permeation measurement.

1.3 Polymer-layered silicate membranes

A polymer matrix, which can sustain high temperature, was tried instead of the silica matrix so as to fabricate films with another type of layered silicate (other than MCM-22). A certain amount of layered silicate was mixed with polymer in solvent. After stirring, membranes were made on a flat glass by evaporating off the solvent.

2. Permeation Testing

Single gas permeation of various gases through: (1) multi-layered mesoporous silica-MCM-22 films, made by a sonication-assisted method; (2) dip-coated mesoporous silica-MCM-22 films; and (3) polymer composite membranes with another layered silicate, other than MCM-22, were measured. The schematic of single gas permeation set-up is shown in Figure 2. 200~250 ml/min of single gas (He, H_2, N_2, and O_2) were fed to one side (retentate) of the permeation cell, the other side (permeate) of which was under vacuum. Since the retentate side was open to ambient air, 1 atm pressure difference was maintained between the feed side and the permeate side. The pressure in the permeate side was measured by use of a pressure transducer and continuously recorded in a computer. The ideal gas law was used to estimate the molar flow rate across the membranes from the recorded pressure. The permeance is calculated according to the following equation,

$$P = \frac{dp}{dt}\frac{V}{RT}\frac{1}{A}\frac{1}{\Delta p} \quad \left(\text{in} \quad \frac{mol}{\sec \cdot m^2 \cdot Pa}\right)$$

where dp/dt is the rate of pressure change in the permeate side, V is the volume of the permeate side, R is the ideal gas constant, T is temperature, A is the cross-sectional area of the membrane, and Δp is the pressure difference across the membrane.

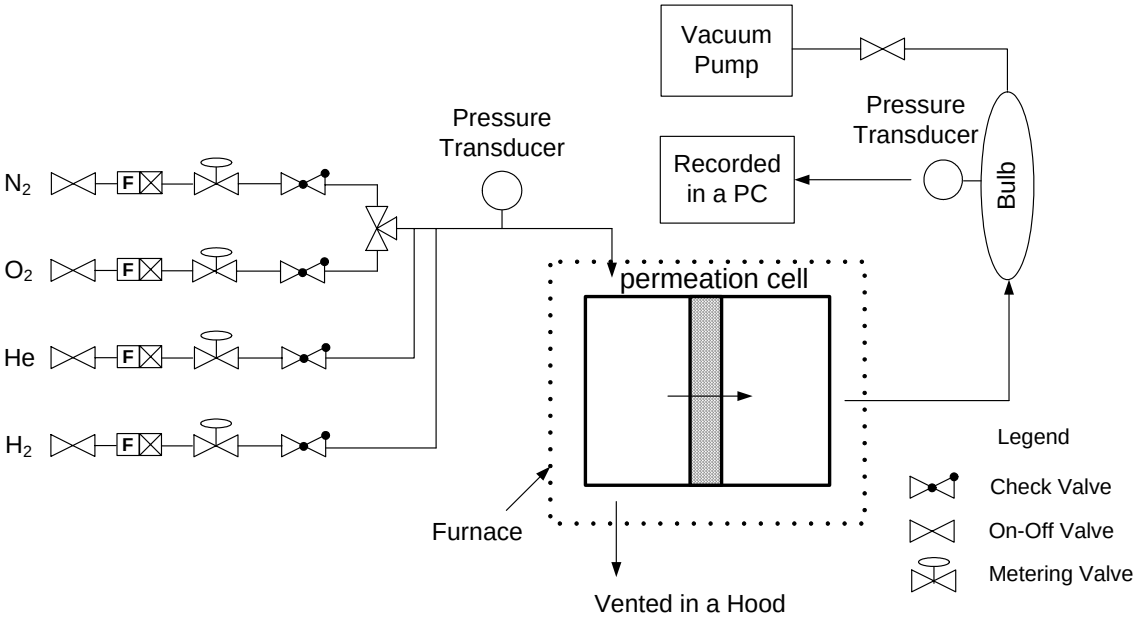

Figure 2. A schematic of single gas permeation measurement set-up.

Results and Discussion

1. Multi-layered mesoporous silica-MCM-22 films

A typical SEM image of 2-time-coated mesoporous silica-MCM-22 films is shown in Figure 3.

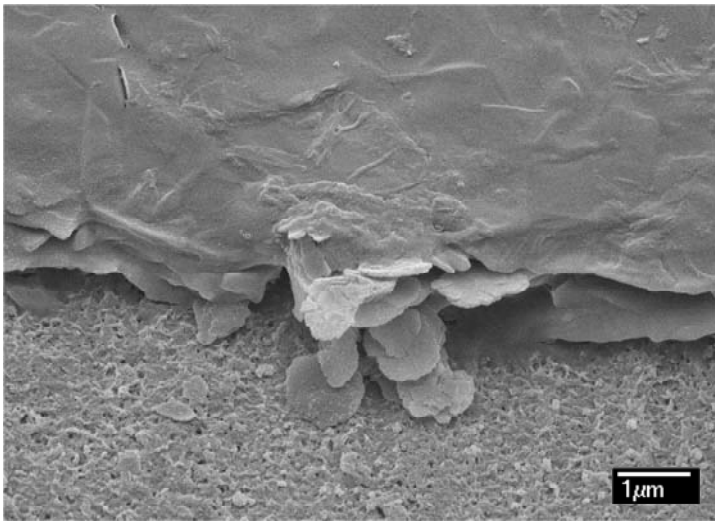

Figure 3. SEM of a 2-time-coated mesoporous silica-MCM-22 film in tilted view.

It appears that MCM-22 particles are embedded in the mesoporous silica matrix. The films formed by a sonication-assisted method are so thin that more dilute silica sol can be used to close gaps in-between MCM-22 particles. At the same time, it was observed that another intermediate layer, γ-Al_2O_3, on macroporous α-Al_2O_3 discs also accommodated a uniform and closely-packed MCM-22 layer.

Single gas permeation measurements were done through 1- and 2-time-coated mesoporous silica-MCM-22 films as seen in Figures 4 and 5, respectively. First, a 1-time-coated mesoporous silica-MCM-22 film exhibits almost the same behavior as a bare α-Al_2O_3 disc (not shown here) with only minor difference being the smaller permeances than those through supports. Since Knudsen diffusion is dominant in this film, permeance is monotonically decreased with temperature, while ideal selectivities are almost fixed as determined mainly by the ratio of molecular weights of two gases (Figure 4).

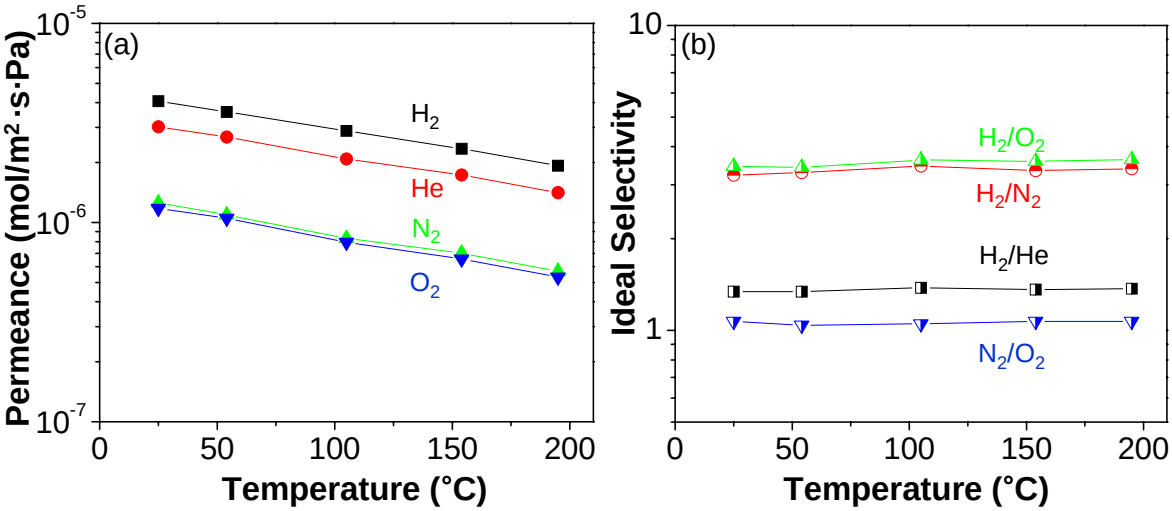

Figure 4. (a) Permeances of single gases through a 1-time-coated mesoporous silica-MCM-22 film and (b) corresponding ideal selectivities.

However, one additional layer to the 1-time-coated mesoporous silica -MCM-22 film (namely, a 2-time-coated mesoporous silica-MCM-22 film) gives a distinct separation performance compared to bare α-Al_2O_3 and the 1-time-coated mesoporous silica -MCM-22 film (Figure 5). It is evident that an additional H_2-selective transport mechanism becomes important along with Knudsen diffusion. The permeance of He almost caught up with that of H_2 and the flux of O_2 rose relatively faster than that of N_2 unlike the behavior shown in Figure 4. In addition, permeances of all the measured gases were reduced compared to supports, while ideal selectivities were increased for smaller sized gases. From the current findings, we expect that films with additional MCM-22 and mesoporous silica layers will exhibit further improvements in H_2 selectivity.

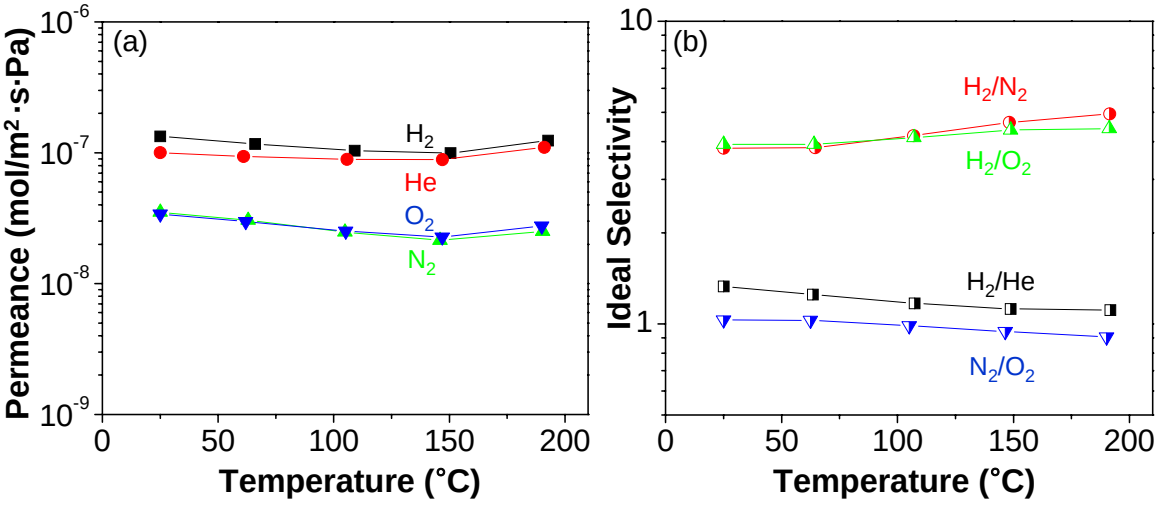

Figure 5. (a) Permeances of single gases through a 2-time-coated mesoporous silica-MCM-22 film and (b) corresponding ideal selectivities.

2. Dip-coated mesoporous silica-MCM-22 films

We also evaluated a simpler way (dip-coating) to eliminate the need for repetitions of MCM-22 deposition followed by mesoporous SiO_2 coating and calcination. The slurry for dip-coating was made by mixing and sonicating calcined and functionalized MCM-22 with silica sol. The surface of calcined MCM-22 was already treated with an agent to be appropriately charged under the silica sol conditions. α-Al_2O_3 discs are used to develop dip-coating conditions before we perform more experiments on tubular supports. One polished side of α-Al_2O_3 discs was dip-coated with the aforementioned slurry. The surface after 7 times repetitions of dip-coating is shown in Figure 6. It seems that some extent of coverage was achieved by several repeated dip-coatings. However, the permeation result from an 8-time-dip-coated mesoporous silica-MCM-22 film does not show any separation improvement for H_2 gas probably because of the discontinuous coverage of the film (Table 1). It appears that this is not a promising approach and will not be pursued further in the near future.

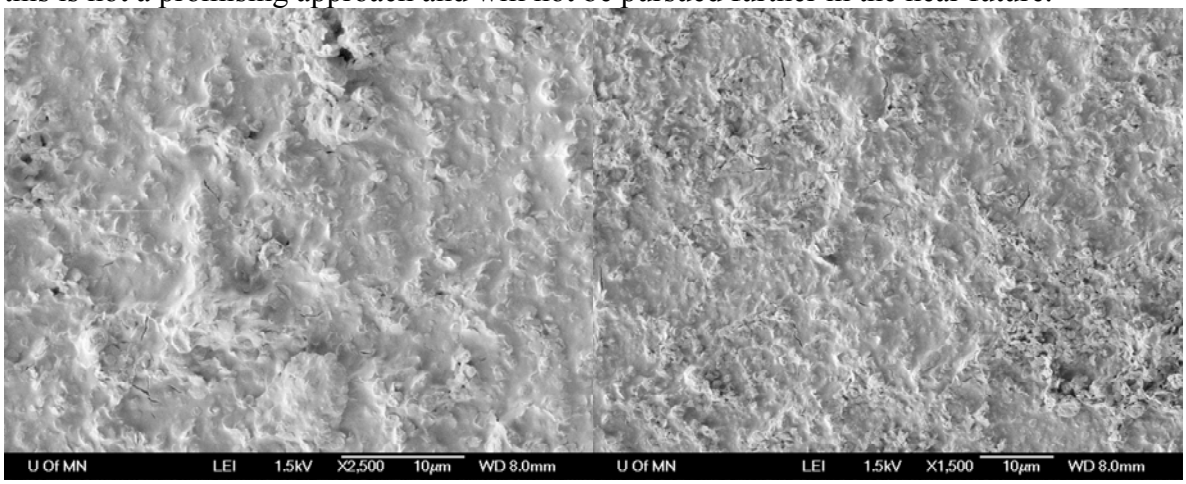

Figure 6. SEM images of the surface of α-Al_2O_3 disc after 7 times dip coating.

Table 1. Single gas permeation through an 8-time-dip-coated mesoporous silica-MCM-22 film on α-Al_2O_3 disc.

Temp. (°C)	Permeance (mol/m^2.Pa·s) × 10^7			Selectivity		
	H_2	N_2	O_2	H_2/N_2	H_2/O_2	N_2/O_2
25	35	10	9.4	3.5	3.7	1.1
100	25	6.5	6.1	3.8	4.0	1.1
150	17	4.6	4.3	3.7	3.9	1.1
200	13	3.3	3.1	3.8	4.0	1.1
25*	46	13	12	3.5	3.7	1.1
100*	30	8.5	7.9	3.6	3.9	1.1
200*	18	5.0	4.6	3.7	4.0	1.1

* Permeation measurement through α-Al_2O_3 disc (no mesoporous silica-MCM-22 films)

3. Polymer-layered silicate membranes

Recently, we started the synthesis of another layered silicate, other than MCM-22. This layered material has potential as selective layer as well. It has a pore opening determined by 8 SiO_4 tetrahedra (8 member ring), whose size is larger than that of the 6-member ring present in MCM-22 structure. The SEM images of the layered silicate and swollen material are shown in Figure 7.

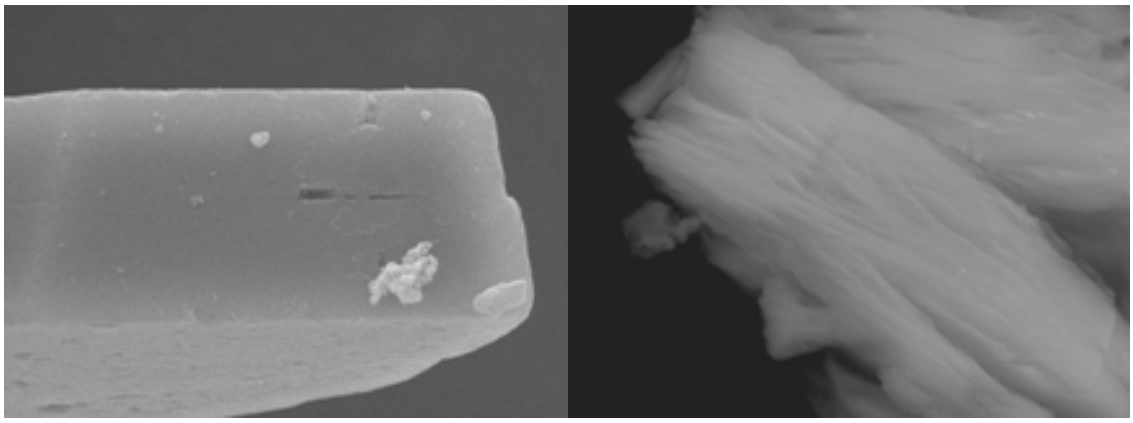

Figure 7. SEM image of the original layered silicate (left) and the swollen material that shows the vestiges of layered structure (right).

The swollen derivative of the layered silicate was blended with a polymer, stable at high temperature, for H_2-selective membranes. We refer to these membranes as polymer-layered silicate membranes. In such a membrane, swollen particles are dispersed in a polymer matrix and this structure may give gas selective capability based on the difference of molecular sizes. In principle, the idea for multi-layered mesoporous silica-MCM-22 films is extended to the polymer-layered silicate membranes. SAXS and SEM data given in Figure 8 indicate good dispersion of the swollen derivative of the layered silicate in the polymer matrix.

The polymer-layered silicate membranes, as well as pure polymer films, were examined by single gas permeation. Table 2 summarizes the permeabilities of H_2 and CO_2 gases along with corresponding ideal selectivities. In general, permeabilities were increased with temperature. In fact, the permeabilities of both H_2 and CO_2 through 2 wt % polymer-layered silicate membranes exceeded that of pure polymer films by ~ 20 % at temperature greater than 100°C. Regarding ideal selectivity, we can see the separation improvement by a factor of 2 with ~ 2 wt % polymer-layered silicate membranes around room temperature. Based on the current findings, we are attempting to look for optimal conditions for H_2-selective membranes. Furthermore, we are trying to increase the number of layers in the membranes by means of exfoliation to improve the separation performance at high temperature.

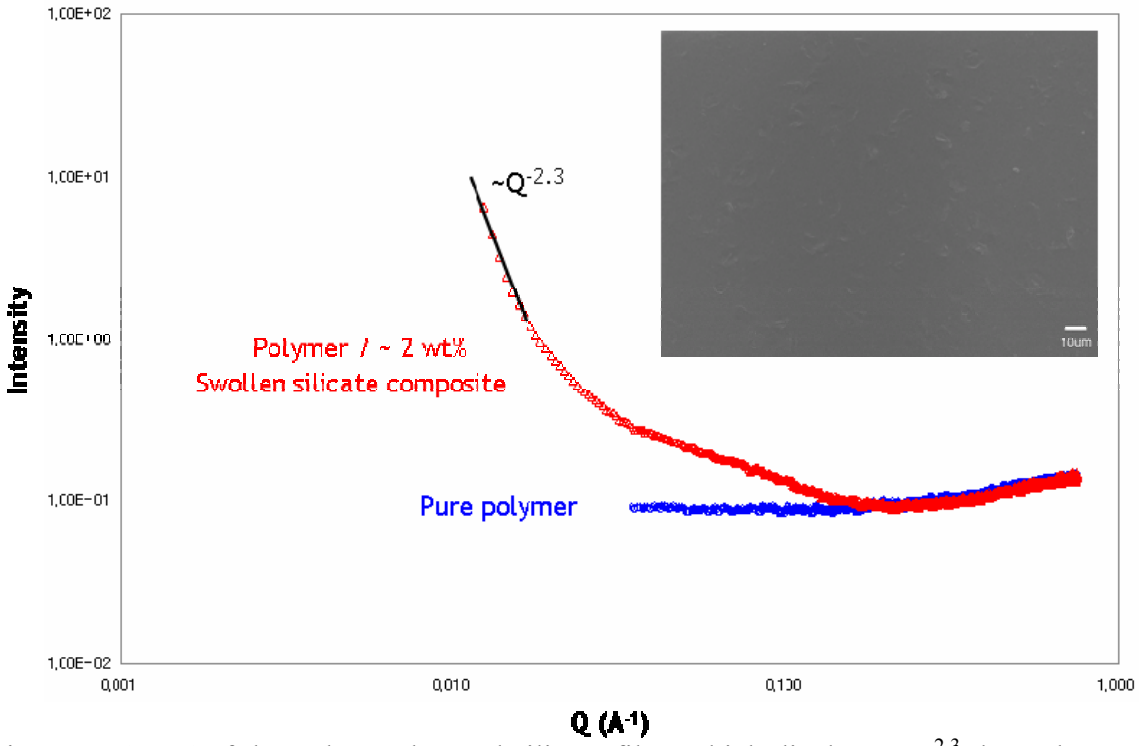

Figure 8. SAXS of the polymer-layered silicate film, which displays $\sim Q^{-2.3}$ dependence and no Bragg peak. The SEM top view of the corresponding film is shown in the inset, which suggests good dispersion of particles (white) in the polymer matrix (dark).

Table 2. Permeability of H_2 & CO_2 for polymer-layered silicate membranes and corresponding ideal selectivity measured at different temperatures.

Temp (°C)	Permeability (Barrer)				Ideal Selectivity	
	Pure polymer		~2 wt% composite		Pure polymer	~2 wt% composite
	H_2	CO_2	H_2	CO_2	H_2 / CO_2	H_2 / CO_2
35	1.92	0.09	0.92	0.03	21.55	35.45
100	6.51	0.29	6.75	0.37	22.26	18.09
200	17.06	0.89	20.14*	1.12	19.17	17.91

* The permeability of H_2 in barrer is equivalent to flux ~ 0.01mol/m^2·s assuming 0.05μm thickness at 1 atmosphere pressure difference.

Conclusions

At first, on the basis of current findings, multi-layered MCM-22 films by a sonication-assisted method seem promising in the sense that only 2-time-coated mesoporous silica-MCM-22 films show monotonically rising ideal selectivity as temperature is increased. The observed selectivity for hydrogen over other gases is larger than the one expected from Knudsen type diffusion. Secondly, a simple dip-coating approach was also attempted. However, in the dip-coating approach, we could not obtain separation improvement possibly due to the discontinuous coverage of the supports. Finally, polymer-layered silicate membranes were fabricated by blending a layered silicate with a polymer matrix, which is stable at high temperature. The polymer-layered silicate membranes resulted in good separation performance at room temperature. No separation improvement was evident at higher temperatures, at which only a small increase in flux was established. Since the primary goal of this project is high temperature H_2-selective membrane fabrication, more extensive study will be continued to improve the separation performance at high temperature.

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The following two publications acknowledge partial support from this award.

Langmuir 22, 5217-5219 (2006) (with Lee JA, Meng L, Norris DJ, and Scriven LE) Colloidal Crystal Layers of Hexagonal Nanoparticles by Convective Assembly

Chemistry of Materials, Accepted (2006) (with Karanikolos GN, Wydra JW, Stoeger J, Corma A, and Hermenegildo G) Continuous c-Oriented $AlPO_4$-5 Films by Tertiary Growth

List of Acronyms and Abbreviations

SEM : Scanning Electron Microscopy

SAXS : Small Angle X-ray Scattering